

What is claimed is:

1. A composition for use in forming a porcelain enamel coating having a metallic appearance, said composition including a glass component comprising a glass frit, said glass frit comprising by weight: about 45% to about 55% SiO₂, about 4 to about 20% R₂O, about 9 to about 15% B₂O₃, about 4 to about 12% MnO₂, about 1.5 to about 7% F₂, about 0% to about 20% MO₂, about 0% to about 10% RO, about 0% to about 6% NO₂, about 0% to about 2% P₂O₅, about 0% to about 3% CoO, about 0% to about 3% NiO, about 0% to about 3% Al₂O₃, about 0% to about 3% Fe₂O₃, about 0% to about 3% CuO, about 0% to about 4% ZrO₂, about 0% to about 2% Nb₂O₅, and about 0% to about 5% Sb₂O₃, wherein R₂O represents at least one alkali oxide, wherein RO represents at least one alkaline earth oxide and wherein M represents at least one transition metal.
2. The composition of claim 1, wherein R₂O is selected from the group consisting of Na₂O, Li₂O and K₂O, or combinations thereof.
3. The composition of claim 1 wherein MO₂ is selected from the group consisting of ZrO₂, SnO₂, TiO₂ and CeO₂.
4. The composition of claim 1 wherein RO is selected from the group consisting of MgO, CaO, SrO, and BaO.
5. The composition of claim 1 further comprising an oxide pigment, selected from the group consisting of iron brown hematite; cobalt silicate blue olivine; nickel barium titanium primrose priderite; lead antimonite yellow pyrochlore; nickel antimony titanium yellow rutile; nickel niobium titanium yellow rutile; nickel tungsten yellow rutile; chrome antimony titanium buff; chrome niobium titanium buff rutile; chrome tungsten titanium buff rutile; manganese antimony titanium

buff rutile; titanium vanadium antimony grey rutile; manganese chrome antimony titanium brown rutile; manganese niobium titanium brown rutile; cobalt aluminate blue spinel; zinc chrome cobalt aluminum spinel; cobalt chromate blue-green spinel; cobalt titanate green spinel; iron chromite brown spinel; iron titanium brown spinel; nickel ferrite brown spinel; zinc ferrite brown spinel; zinc iron chromite brown spinel; copper chromite black spinel; iron cobalt chromite black spinel; chrome iron manganese brown spinel; chrome iron nickel black spinel; chrome manganese zinc brown spinel; nickel manganese iron chromium black; tin vanadium yellow cassiterite; chrome tin orchid cassiterite; chrome tin pink sphene, and combinations thereof.

6. The composition of claim 1 further comprising a crystalline component wherein the crystalline component comprises additives selected from the group consisting of TiO_2 , ZrSiO_4 , Zn_2SiO_4 , $\text{Bi}_{12}\text{SiO}_{20}$, $\text{Bi}_4(\text{SiO}_4)_3$, and Bi_2SiO_5 , $2\text{ZnO} \bullet 3\text{TiO}_2$, $\text{Bi}_2\text{O}_3 \bullet \text{SiO}_2$, $\text{Bi}_2\text{O}_3 \bullet 2\text{TiO}_2$, $2\text{Bi}_2\text{O}_3 \bullet 3\text{TiO}_2$, $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $\text{Bi}_2\text{Ti}_2\text{O}_7$, $\text{Bi}_{12}\text{TiO}_{20}$, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, and $\text{Bi}_2\text{Ti}_4\text{O}_{11}$.
7. The composition of claim 1 further comprising a mill addition selected from the group consisting of mica particles; clays; urea; boric acid, molybdic acid; sodium molybdate; copper chloride, and the chlorides, carbonates, and hydroxides, of sodium, potassium, magnesium, and calcium, and combinations thereof.
8. The composition of claim 1 further comprising a titanium opacified frit wherein the titanium opacified frit comprises by weight: SiO_2 (33-57%), B_2O_3 (0-23%), TiO_2 (13-26%), F_2 (0-9%), NO_2 (1-10%), Na_2O (5-20%), K_2O (0-13%), Li_2O (0-4%), Al_2O_3 (0-6%), AuO (0-0.05%), BaO (0-5%), CaO (0-2.5%), CoO (0-0.05%), MgO (0-1.5%), P_2O_5 (0-4%), Sb_2O_3 (0-1.5%), ZnO (0-23%), and ZrO_2 (0-10%).

9. The composition of claim 8, wherein R₂O is selected from the group consisting of Na₂O, Li₂O and K₂O, and combinations thereof.
10. The composition of claim 8 wherein MO₂ is selected from the group consisting of ZrO₂, SnO₂, TiO₂, and CeO₂.
11. The composition of claim 8 wherein RO is selected from the group consisting of MgO, CaO, SrO, and BaO.
12. The composition of claim 8 further comprising an oxide pigment, selected from the group consisting of iron brown hematite; cobalt silicate blue olivine; nickel barium titanium primrose priderite; lead antimonite yellow pyrochlore; nickel antimony titanium yellow rutile; nickel niobium titanium yellow rutile; nickel tungsten yellow rutile; chrome antimony titanium buff; chrome niobium titanium buff rutile; chrome tungsten titanium buff rutile; manganese antimony titanium buff rutile; titanium vanadium antimony grey rutile; manganese chrome antimony titanium brown rutile; manganese niobium titanium brown rutile; cobalt aluminate blue spinel; zinc chrome cobalt aluminum spinel; cobalt chromate blue-green spinel; cobalt titanate green spinel; iron chromite brown spinel; iron titanium brown spinel; nickel ferrite brown spinel; zinc ferrite brown spinel; zinc iron chromite brown spinel; copper chromite black spinel; iron cobalt chromite black spinel; chrome iron manganese brown spinel; chrome iron nickel black spinel; chrome manganese zinc brown spinel; nickel manganese iron chromium black; tin vanadium yellow cassiterite; chrome tin orchid cassiterite; chrome tin pink sphene, and combinations thereof.
13. The composition of claim 1 further comprising a luster frit, wherein the luster frit comprises by weight: SiO₂ (46-54%), B₂O₃ (15-17%), MnO₂ (8-10%), F₂ (1.7-

3.5%), Na₂O (5-20%), K₂O (2-9%), NO₂ (0-6%), Li₂O (0-4%), Al₂O₃ (0-2%), BaO (0-5%), CaO (0-1%), CoO (0-1%), CuO (0-1%), Fe₂O₃ (0-2%), NiO (0-1%), P₂O₅ (0-3%), and Sb₂O₃ (0-3%).

14. The composition of claim 1 further comprising a clear/semi-opaque frit, wherein the clear/semi-opaque frit comprises: SiO₂ (46-57%), B₂O₃ (11-17%), Na₂O (5-20%), F₂ (1-10%), TiO₂ (0-13%), NO₂ (0-4%), K₂O (0-12%), Li₂O (0-4%), Al₂O₃ (0-3%), BaO (0-5%), CaO (0-3%), MgO (0-1%), P₂O₅ (0-2%), ZnO (0-3%), and ZrO₂ (0-3%).

15. A composition for use in forming a porcelain enamel coating having a metallic appearance, comprising:

- a. an amount (A) of a glass component comprising a metallic appearance frit;
- b. an amount (B) of a second frit selected from the group consisting of luster frits or clear/semi-opaque frits;
- c. wherein the weight ratio of A to B is about 1:1 to about 9:1, and
- d. wherein the metallic appearance frit comprises SiO₂ (45-55%), R₂O (4-20%), B₂O₃ (9-15%), MnO₂ (4-12%), F₂ (1.5-7%), MO₂ (0-20%), RO (0-10%), NO₂ (0-6%), P₂O₅ (0-2%), CoO (0-3%), NiO (0-3%), Al₂O₃ (0-3%), Fe₂O₃ (0-3%), CuO (0-3%), ZrO₂ (0-4%), Nb₂O₅ (0-2%), and Sb₂O₃ (0-5%),
- e. wherein M represents a transition metal; wherein R₂O represents one or more alkali oxides, and wherein RO represents one or more alkaline earth oxides.

16. The composition of claim 15 wherein MO₂ is present in an amount not exceeding about 20 wt%, and wherein MO₂ is selected from the group consisting of ZrO₂, SnO₂, TiO₂, CeO₂, and La₂O₃.
17. The composition of claim 15 wherein the second frit comprises a luster frit, wherein the luster frit comprises: SiO₂ (46-54%), B₂O₃ (15-17%), F₂ (1.7-3.5%), Na₂O (5-20%), K₂O (2-9%), MnO₂ (8-10%), NO₂ (0-6%), Li₂O (0-4%), Al₂O₃ (0-2%), BaO (0-5%), CaO (0-1%), CoO (0-1%), CuO (0-1%), Fe₂O₃ (0-2%), NiO (0-1%), P₂O₅ (0-3%), and Sb₂O₃ (0-3%).
18. The composition of claim 15 wherein the second frit comprises a semi-opaque frit, wherein the semi-opaque frit comprises: SiO₂ (46-57%), B₂O₃ (11-17%), F₂ (1-10%), Na₂O (5-20%), TiO₂ (0-13%), NO₂ (0-4%), K₂O (0-12%), Li₂O (0-4%), Al₂O₃ (0-3%), BaO (0-5%), CaO (0-3%), MgO (0-1%), P₂O₅ (0-2%), ZnO (0-3%), and ZrO₂ (0-3%).
19. The composition of claim 1 wherein the glass frit comprises by weight: about 45% to about 55% SiO₂, about 4 to about 20% R₂O, about 9 to about 15% B₂O₃, about 4 to about 12% MnO₂, about 1.5 to about 7% F₂, and at least one of the following oxides, not to exceed the indicated amount: MO₂ (20%), RO (10%), NO₂ (6%), P₂O₅ (2%), CoO (3%), NiO (3%), Al₂O₃ (3%), Fe₂O₃ (3%), CuO (3%), ZrO₂ (4%), Nb₂O₅ (2%), and Sb₂O₃ (5%), wherein R₂O represents at least one alkali oxide, wherein RO represents at least one alkaline earth oxide and wherein M represents at least one transition metal.
20. An appliance comprising a porcelain enamel coating having a metallic appearance, said coating formed by firing the composition of claim 1.